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Invention **COMPOSITION FOR ANTIREFLECTION COATING AND METHOD FOR FORMING PATTERN**

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PATENT ABSTRACTS OF JAPAN

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(54) SURFACE ANTIREFLECTION COATING COMPOSITION

(57)Abstract:

PURPOSE: To obtain a surface antireflection coating compsn. having a low refractive index, capable of satisfactorily forming and removing a coating film with an aq. medium and suppressing the occurrence of residue by using a water-soluble fluorine compd. contg. a specified compd.

CONSTITUTION: This surface antireflection coating compsn. contains a water-soluble fluorine compd. and water. The fluorine compd. contains one or more kinds of compds. selected from among fluoroalkyl polyether sulfonic acid, its nonmetallic salts, fluoroalkyl polyether carboxylic acid and its nonmetallic salts. The nonmetallic salts mean metal-free salts and include ammonium salts and alkyl substd. ammonium salts such as monoalkyl-, dialkyl- and trialkylammonium salts.

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CLAIMS

[Claim(s)]

[Claim 1] The surface acid-resisting spreading constituent characterized by containing one or more compounds chosen from the group to which a water-soluble fluorine compound becomes a fluorination alkyl polyether sulphone acid and its nonmetallic salt, and a list from a fluorination alkyl polyether carboxylic acid and its nonmetallic salt in the surface acid-resisting spreading constituent containing a water-soluble fluorine compound and water.

[Claim 2] The surface acid-resisting spreading constituent according to claim 1 characterized by containing further one or more compounds chosen from the group which becomes a fluorination alkyl sulfonic acid and its nonmetallic salt, and a list from a fluorination alkyl carboxylic acid and its nonmetallic salt.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the charge of pattern formation in photolithography in the micro-processing method in creation of a semiconductor device etc.

[0002]

[Description of the Prior Art] If the ultra-fine processing technology represented by manufacture of an integrated circuit etc. is raising the process tolerance increasingly in recent years and dynamic random access memory (DRAM) is taken for an example, in current, the submicron processing technique is established as a technique of mass-production-method level. The photolithography technique which used the light of short wavelength, such as g line (436nm), i line (365nm), and KrF excimer laser light (248nm), is used for this submicron processing. With these photolithography techniques, although a photoresist constituent is used, amelioration is repeated also for this photoresist constituent and the highly efficient photoresist constituent is proposed variously.

[0003] Although it has higher definition of course as a property required of this photoresist constituent, it is important not to change the dimension of the imprinted pattern by the spreading thickness of a photoresist constituent. However, in photolithography, in order to be influenced of an optical interference, there was a limitation in reducing dimension fluctuation of the pattern to fluctuation of the thickness of a resist.

[0004] That is, since the light irradiated is usually the homogeneous light, the light by which incidence was carried out into the photoresist film repeats a film Uchida pile echo in the interface of the upper and lower sides of the photoresist film. Consequently, by interferential action, since the effect--as a matter of fact quantity of light changed with spreading thickness, the measurement of the pattern imprinted changed periodically according to fluctuation of spreading thickness, and the limitation was in the dimensional accuracy of a pattern.

[0005] As the technique of solving this trouble, an antireflection film is made to form on the photoresist film, effect of the above-mentioned film Uchida pile echo is made small, and the method of raising a dimension controllability is proposed (JP,60-149130,A, JP,62-62520,A, JP,62-62521,A, JP,5-188598,A, etc.). The photoresist film is transparent film with a different refractive index, and by choosing the thickness and refractive index suitably, the antireflection film makes an optical interference cause effectively, and makes small effect of a film Uchida pile echo.

[0006] Drawing 1 is the typical sectional view showing the principle of relief of the film Uchida pile echo by the antireflection film. The photoresist film 22 is formed on the substrate 23 which should be processed, and the antireflection film 21 is further formed on the photoresist film 22. The exposure light 20 penetrates the antireflection film 21 and the photoresist film 22, reaches a substrate 23, and is reflected with a substrate 23. It arrives at the interface 26 of the antireflection film 21 and the photoresist film 22, the part is reflected (the 2nd reflected light 27), and the remainder penetrates the 1st reflected light 24. A part of transmitted light is reflected further in the interface 25 of an antireflection film 21 and its outside (the 3rd reflected light 28). By besides making the 2nd reflected light 27 of an

account, and the 3rd reflected light 28 cause interference, it becomes possible to make that reinforcement small.

[0007] However, there are various problems which are described below in the conventional acid-resisting spreading constituent. Although it is desirable it not only to make [1st] thickness of an antireflection film into odd times of $(\lambda/4n)$ (λ expresses the wavelength of exposure light and n expresses the refractive index of an antireflection film), but to use as the square root of the refractive index of the photoresist film the refractive index of the surface acid-resisting spreading constituent which forms an antireflection film, there was a problem that a limitation was in this refractive index.

[0008] Namely, generally, although the desirable refractive index of an acid-resisting spreading constituent becomes 1.27 to about 1.3 since the refractive index of the photoresist film is 1.6 to about 1.7 It is [consequently] very desirable industrially that the dissolution clearance also of the antireflection film can be carried out with the developer of the aqueous medium currently generally [in order not to make the process of the spreading-exposure-development of the photoresist which the conventional photolithography technique took change] on the other hand used. To an acid-resisting spreading constituent To be water solubility is also demanded. However, the refractive index of the water-soluble acid-resisting spreading constituent known now is about 1.4, and has not reached the value of the above low refractive indexes.

[0009] Even if it was a low refractive index, the grain-like foreign matter was generated in the film between the short time after spreading (for example, less than 24 hours), and the problem of being in the condition that there is nothing to an activity **** was also in the 2nd. Moreover, after antireflection-film formation, when development of the photoresist film was performed, since the residue after development (Society for Cutting Up Men) occurred in the 3rd mostly, the problem that there was no **** in practical use was also in it.

[0010]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the surface acid-resisting spreading constituent which is a low refractive index (1.4 or less), and formation and clearance could do the spreading film good by the water medium, and was excellent in the comprehensive target with very little generating of residue (Society for Cutting Up Men) in view of the aforementioned background.

[0011]

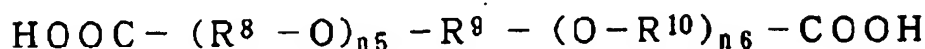
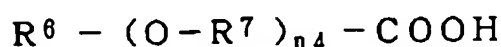
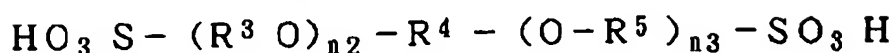
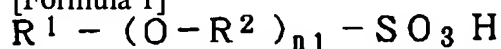
[Means for Solving the Problem] When using the surface acid-resisting spreading constituent using a specific compound as a result of this invention persons' repeating examination variously in order to attain the above-mentioned object, a header and this invention were completed for the ability of the above-mentioned object to be attained. That is, the summary of this invention consists in the surface acid-resisting spreading constituent characterized by containing one or more compounds chosen from the group to which a water-soluble fluorine compound becomes a fluorination alkyl polyether sulphone acid and its nonmetallic salt, and a list from a fluorination alkyl polyether carboxylic acid and its nonmetallic salt in the surface acid-resisting spreading constituent containing a water-soluble fluorine compound and water.

[0012] Hereafter, it explains to a detail per this invention. In this invention, it makes it indispensable to contain at least one sort chosen as a surface acid-resisting spreading constituent from a fluorination alkyl polyether carboxylic acid and its nonmetallic salt by a fluorination alkyl polyether sulphone acid and its nonmetallic salt, and the list as a water-soluble fluorination compound.

[0013] Although there is especially no limit in the amount used, it is 2% or more still more preferably 1% or more preferably to total constituent weight, and is 5% or less still more preferably 10% or less preferably. The poly vinyl alcohol and polyacrylic acid which are generally known, and polyvinylpyrrolidone are not enough as a refractive index. Typically as the fluorination alkyl polyether sulphone acid used by this invention, and a fluorination alkyl polyether carboxylic acid, the compound which has the following general formula is mentioned.

[0014]

[Formula 1]



[0015] (However, R1 and R6 express the alkyl group by which a part or all of a hydrogen atom is permuted by the fluorine atom among the above-mentioned formula, respectively.) R2 -R5 And R7 -R13 express the alkylene group by which a part or all of a hydrogen atom is permuted by the fluorine atom, respectively. You may differ, even if two or more R2, R3, R5, R7, R8, and R10, R11 and R13 are the same respectively. R3 [moreover,] And R5 and R8 And you may differ, even if the same at the intramolecular respectively same about R10, R11, and R13, and n1-n8 express one or more integers, respectively.

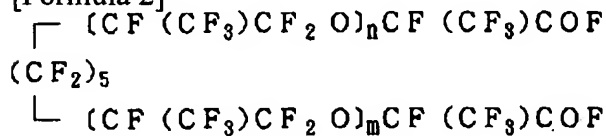
In addition, it is R1 here. And R6 For the carbon number of an alkyl group, the carbon number of the alkylene group of one to about 20, R2 and R3, R5, R7, R8, and R10, R11 and R13 is usually one to about 5, R4, and R9. And the carbon number of the alkylene group of R12 is usually one to about 20.

[0016] By this invention, the above sulfonic acids and carboxylic acids can also be used in the form of a nonmetallic salt. In this description, a nonmetallic salt means the salt which does not contain a metal. As a nonmetallic salt of the above-mentioned sulfonic acid or a carboxylic acid, the ammonium salt which may be permuted by alkyl groups, such as ammonium salt, monoalkyl ammonium salt, dialkyl ammonium salt, a trialkylammonium salt, and tetra-alkyl ammonium salt, is mentioned, for example. As an alkyl group which constitutes the above-mentioned salt, a with a carbon number of about one to three alkyl group may be mentioned, among those a part or all of a hydrogen atom may usually be permuted by the fluorine atom. When the metal salt of the above-mentioned sulfonic acid or a carboxylic acid is used, a metal may pollute the processed material (substrate) which should be processed and it is not desirable.

[0017] It is desirable to use a fluorination alkyl polyether sulphone acid and/or its nonmetallic salt in this invention. Although there is especially no limit as long as the molecular weight of the above-mentioned fluorination alkyl polyether sulphone acid or its salt, or a fluorination alkyl polyether carboxylic acid or its salt agrees for the object, it is usually [300 or more] 50000 or less preferably 500 or more and usually [100000 or less]. Moreover, two or more kinds may use these, mixing. As an example of such a water-soluble fluorine compound E.I.du marketed as a reagent from Aldrich Sulfonic acids, such as perfluoroalkyl polyether sulfonate named Nafion made from Pont (trademark) generically Perfluoro-- 2, 5, 8, 11-tetramethyl - 3, 6, 9, a 12-tetra-OKISA pentadecane acid, Perfluoro-- 2, 5, 8-trimethyl -3, 6, 9-trioxadodecanoic acid, and PCR Carboxylic acids, such as dicarboxylic acid which is the hydrolysis product of the perfluoropolyether diacid fluoride marketed as a reagent from Inc., are mentioned. In addition, the above-mentioned perfluoropolyether diacid fluoride is the compound of the following structures.

[0018]

[Formula 2]



[0019] (However, m+n=3 or m+n=4.)

The water-soluble above-mentioned fluorine compound can make the two or more sorts contain.

Although the constituent of this invention may contain only an above-mentioned compound and water, it is desirable to contain water-soluble fluorine compounds other than the above in order to reduce a refractive index further. As this water-soluble fluorine compound, fluorination alkyl sulfonic acids, such as a perfluoro-alkyl sulfonic acid and a perfluoro-alkyl carboxylic acid, and a fluorination alkyl carboxylic acid are mentioned, and, specifically, Monod of 4-20, a G sulfonic acid and Monod, or a G carboxylic acid is mentioned for carbon numbers, such as a perfluoro-octane sulfonic acid, a perfluoro-decane sulfonic acid, a perfluoro-octanoic acid, a perfluoro-decanoic acid, a perfluoro-glutaric acid, and perfluoro-sebacic acid. Especially in this, a sulfonic-acid compound is desirable. Moreover, the salt of the ammonium which can also use these nonmetallic salts, for example, may be permuted by alkyl groups, such as ammonium salt, monoalkyl ammonium salt, dialkyl ammonium salt, a trialkylammonium salt, and tetra-alkyl ammonium salt, is mentioned concretely.

[0020] As an alkyl group which constitutes the above-mentioned salt, the alkyl group of carbon numbers 1-3 is desirable, and a part or all of a hydrogen atom may be permuted by the fluorine atom before long. When the metal salt of the above-mentioned sulfonic acid or a carboxylic acid is used, a metal may pollute the processed material (substrate) which should be processed and it is not desirable. In addition, the two or more sorts can also be made to contain from the group which becomes an above-mentioned perfluoro-alkyl sulfonic acid and its above-mentioned nonmetallic salt list from a perfluoro-alkyl carboxylic acid and its nonmetallic salt.

[0021] Since a refractive index falls, more ones of the content of the water-soluble fluorine compound which these pans are made to contain are desirable, but since the problem of being unable to form the good spreading film may occur when many [too], it is usually 90% or less preferably 95% or less to total-solids weight.

[0022] Although water is used for the constituent of this invention as a solvent, in order to raise the solubility of a fluorine compound, the aquosity mixed solvent of the organic solvent and water which can be mixed with water, such as low-grade alkyl carboxylic acids, such as lower alcohol, such as a methanol, ethanol, and propanol, and an acetic acid, may be used for it. In this case, since the lower layer photoresist film may be dissolved when there are too many mixed rates of an organic solvent, that amount used is usually 20 or less % of the weight preferably 30 or less % of the weight to all solvents.

[0023] In order to raise the stability of the spreading film which made form it and formed the good spreading film in the constituent of this invention in addition to the above-mentioned compound, it is possible to also make a water-soluble liquefied fluorine compound live together. These water-soluble liquefied fluorine compounds are used as a solvent, 50 degrees C or more of 80 degrees C or more of boiling points in one atmospheric pressure are 90 degrees C or more still more preferably preferably, and above 0 degree C, it is a water-soluble liquefied fluorine compound, and, specifically, fluoro alkyl sulfonic acids, such as fluoro alkyl carboxylic acids, such as fluoro alkyl alcohols, such as trifluoro ethanol, tetrafluoro propanol, and octafluoro amyl alcohol, and gifblaar poison, and trifluoro methansulfonic acid, are mentioned. Especially in this, with a carbon number of six or less fluoro alkyl alcohols are desirable. Although the higher one of the solubility to the water of these water-soluble liquefied fluorine compounds is desirable, if it dissolves in the above-mentioned aquosity mixed solvent, it will not interfere practically. Although it is not necessary to make this water-soluble liquefied fluorine compound not necessarily contain in the constituent of this invention, it is desirable to make it contain, in order to raise the stability of the spreading film and to attain a lower refractive index. since there is no improvement of effectiveness even if problems, such as an upper limit being not only in an improvement of effectiveness, but spoiling the description of the spreading film even if many [too], may occur as amount of the water-soluble liquefied fluorine compound used and it is too few -- usually -- all solvent components -- receiving -- 0.1 - 10 % of the weight -- it is used one to 6% of the weight still more preferably 0.5 to 8% of the weight preferably.

[0024] Although the constituent of this invention can also add the compound which has low refractive indexes, such as other fluorine systems, the low refractive-index compound in this case is fusibility at the above-mentioned medium, and, as for that mixing percentage, it is desirable that it is 20 or less % of the weight to total solids. In the constituent of this invention, in order to improve spreading nature etc.

further, a surfactant etc. may be added. Moreover, an extinction agent can also be added in order to make small effect of the above-mentioned film Uchida pile echo.

[0025] The surface acid-resisting spreading constituent of this invention is usually applied on the photoresist film applied on the substrate, and acts as an antireflection film. After the photoresist film is exposed through an antireflection film and a pattern is imprinted, a pattern is formed of development. All the photoresist constituents using the homogeneous light as a photoresist constituent for making the photoresist film form can be used theoretically. That is, the photoresist constituent for the conventional g line, i line, and excimer laser light (248nm, 193nm) can be used, and either a positive type or a negative mold can be used as an ingredient.

[0026] As a concrete photoresist constituent, the photoresist constituent of the optical bridge formation mold of ** Pori cinnamic acid vinyl system and a polyisoprene cyclized-rubber system (Society of Synthetic Organic Chemistry, Japan, the 42nd volume, No. 11, 979 etc. pages, etc.), ** the thing (Society of Synthetic Organic Chemistry, Japan -- 979 pages No. 11 the 42nd volume) which comes to dissolve 1 and 2-naphthoquinonediazide system sensitization agent and alkali fusibility resin in an organic solvent Or it depolymerizes. the acid or base generated in ** light exposures, such as JP,62-136637,A and JP,62-153950,A, -- a polymerization -- The so-called chemistry magnification mold photoresists (JP,59-45439,A, JP,4-136860,A, JP,4-136941,A, etc.) which discover the engine performance of a photoresist are mentioned.

[0027] ** As resin used for a photoresist constituent, polyvinyl alcohol, the Pori cinnamic acid vinyl resin manufactured from cinnamic acid chloride, and the cyclized-rubber system resin which uses 1 and 4-cis- polyisoprene as a principal component are mentioned. Moreover, photoinitiator cross linking reagents, such as 4 and 4'-diazido chalcone, 2, and 6-G (4'-azide benzylidene) cyclohexanone, may be added if needed.

[0028] ** As a 1 used for photoresist constituent, and 2-naphthoquinonediazide system sensitization agent, a 1 of compound which has phenolic hydroxyl group, 2-benzoquinone diazido-4-sulfonate derivative, 1, 2-naphthoquinonediazide-4-sulfonate derivative, 1, and 2-naphthoquinonediazide-5-sulfonate derivative etc. is mentioned. Here, as a compound which has a phenolic hydroxyl group, polyphenol, novolak resin, etc. which are manufactured from polyhydroxy benzoates, such as polyhydroxy benzophenones, such as 2, 3, and 4-trihydroxy benzophenone, and gallic-acid ethyl, phenols, and aldehydes are mentioned.

[0029] ** The polymers to which the polymerization of this was carried out as alkali fusibility resin used for a photoresist constituent by making into a monomer the novolak resin to which the polycondensation of a phenol derivative and the aldehyde derivative was carried out, an acrylic-acid derivative, a cinnamic acid derivative, a styrene derivative, a maleic-acid derivative, etc. are mentioned.

[0030] ** It consists of resin which has an unstable radical to acids, such as Pori (p-tert-butoxycarbonyloxy) styrene, as a photoresist constituent, and a compound which generates an acid by the optical exposure of triphenylsulfonium hexafluoro ASENATO etc., and the photoresist constituent which the optical exposure section solubilizes or insolubilizes to a developer is mentioned. Moreover, it consists of novolak resin to which the polycondensation of a phenol derivative and the aldehyde derivative was carried out, and a compound which generates an acid by the optical exposure of an alkoxy methylation urea, halogenation methyl triazine, etc., and the photoresist constituent which the optical exposure section insolubilizes to a developer is mentioned.

[0031] Although a photoresist constituent usually contains an organic solvent As an organic solvent, for example Acetic-ester; ethylcellosolve [, such as aromatic hydrocarbon; ethyl acetate,], such as toluene and a xylene, etc., The monochrome or G alkyl ether of monochrome or G ethylene glycol; Propylene glycol monomethyl ether etc., The monochrome or G alkyl ether of monochrome or G propylene glycol; Propylene-glycol-monomethyl-ether acetate etc., Alkyl cellosolve acetates; Ester; methyl ethyl ketones, such as ethylene carbonate and gamma-butyrolactone, Ketones, such as 2-heptanone and cyclopentanone; as for hydroxy , alkoxy **, such as ethyl lactate, 3-methoxy methyl propionate, and pyruvic-acid ethyl, oxy-alkyl carboxylic-acid alkyl ester; etc. is mentioned.

[0032] These solvents are suitably chosen in consideration of the solubility of resin or a sensitization

agent, the stability of a photoresist constituent, etc. Moreover, these photoresist constituents may contain the surfactant for spreading nature amelioration, the sensitizer for the improvement in sensibility, etc. if needed. Although not limited especially as a substrate used for pattern formation, substrates for IC manufacture, such as a silicon substrate and a gallium arsenide substrate, are common.

[0033] There is especially no limit in the approach of applying a photoresist constituent on a substrate, and the approach of applying an acid-resisting spreading constituent on the photoresist film, a spin coater etc. is used, and it is carried out according to a conventional method. The thickness of the obtained photoresist constituent is usually about 0.3-5.0micro. After applying to the substrate top of a photoresist constituent, stoving processing may be performed, and it is usually carried out for 30 - 120 seconds at 70-100 degrees C using a hot plate etc.

[0034] What is necessary is just to optimize the thickness of an antireflection film suitably with exposure wavelength etc. according to the principle of the above-mentioned acid resisting. the antireflection film formed when a water-soluble constituent was used as a constituent for forming an antireflection film -- the time of the development after exposure and in an alkali water solution -- or it is easily removable by only rinsing.

[0035] As exposure wavelength used for performing an image imprint on the photoresist film formed on the substrate, g line (436nm), i line (365nm), XeCl excimer laser light (308nm), KrF excimer laser light (248nm), ArF excimer laser light (193nm), etc. are usually effective. Exposure afterbaking (PEB) may be performed after exposing the photoresist film and an antireflection film if needed. The conditions for about 60 - 120 seconds are suitably used at 90-120 degrees C, using a hot plate etc. as conditions for PEB. Although a convection oven may be used instead of a hot plate, time amount longer than the case where a hot plate is usually used in this case is needed.

[0036] As an alkali water solution for developing a photoresist after exposure A, sodium hydroxide, a potassium hydroxide, a sodium carbonate, aqueous ammonia, Inorganic alkali, such as a sodium silicate and a meta-sodium silicate, ethylamine, Secondary amines, such as primary amines, such as n propylamine, diethylamine, and G n propylamine Tertiary amines, such as triethylamine and methyl diethylamine, tetramethylammonium hydroxide, What added alcohol etc. can be used for water solutions, such as quarternary ammonium salt, such as trimethylhydroxyethylammonium hydroxide, or this.

[0037] Moreover, a surfactant etc. can also be added and used if needed. About 15-30 degrees C of developing time are [development temperature] desirable about 30 to 180 seconds. In addition, a photoresist developer is filtered on the occasion of an activity, and it is usually used for it for insoluble matter, removing.

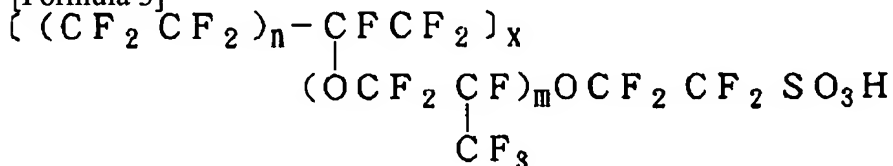
[0038]

[Example] Although an example is given and this invention is explained further below at a detail, this invention is not limited to these examples at all, unless the summary is surpassed.

[0039] The salt which neutralized the example 1 heptadeca fluoro octane sulfonic acid in the tetramethylammonium hydroxide water solution (100% of neutralization indices), and perfluoroalkyl polyether sulfonate (Aldrich reagent; Nafion(trademark)-perfluorinated ion-exchange powder) were mixed by 7:3 by the weight ratio, after dissolving this in water so that it may become 5% of solid content concentration, it filtered with the 0.2-micrometer filter and the surface acid-resisting spreading constituent (A) was prepared. In addition, Above Nafion (trademark) is the water-soluble fluorine compound of the following structures.

[0040]

[Formula 3]



[0041] After carrying out the spin coat of this surface acid-resisting spreading constituent (A) to a silicon wafer with a diameter of 5 inches, heating BEKU was carried out for 60 seconds at 95 degrees C on the hot plate, the paint film was dried, and the spreading film of about 1000A thickness was obtained. The spreading membranous observation result of this spreading film and the measurement result of a refractive index are shown in a table -1. Moreover, this spreading film is dipped in 23-degree C water, and the result of having observed the dissolution detachability of the spreading film is also shown in a table -1.

[0042] After continuing and carrying out the spin coat of the quinone diazide system positive type photoresist (TOKYO OHKA KOGYO [CO., LTD.] CO., LTD. make; TSMR-V90) to a silicon wafer with a diameter of 5 inches, heating BEKU was carried out for 90 seconds at 90 degrees C on the hot plate, the paint film was dried, and photoresist coating of 10350A of thickness was obtained. On this photoresist film, after carrying out the spin coat of the surface acid-resisting spreading constituent (A), heating BEKU was carried out for 60 seconds at 90 degrees C on the hot plate, the paint film was dried, and the photoresist coating wafer with the surface acid-resisting spreading film (700A of thickness) was obtained.

[0043] After exposing this wafer through the mask with a test pattern using g line stepper (GCA company make; DSW-6700B) and performing for [PEB] 90 seconds at 120 degrees C on a hot plate, paddle development was carried out for 60 seconds in 2.38% of the weight of the tetramethylammonium hydroxide water solution. The development omission pattern of 10-micrometer angle in light exposure and the 1-micrometer line & tooth-space pattern with which a 1-micrometer line & tooth space is finished in 1:1 were observed with the scanning electron microscope. A result is shown in a table -1.

[0044] Furthermore it continued, similarly other quinone diazide system positive type photoresists (Mitsubishi Kasei [Corp.] Corp. make; MCPR-i6600), and two or more wafers with which the photoresist film of the thickness to 12000A was formed at intervals of 10000 to every about 100A were obtained. [the wafer] [applied and] The surface acid-resisting spreading constituent (A) was applied to this on the photoresist film like the above at 650A thickness. After exposing this wafer through the mask with a test pattern using i line stepper (;NSRby NIKON CORP. 1755i7A) and performing for [PEB] 90 seconds at 120 degrees C on a hot plate, paddle development was carried out for 60 seconds in 2.38% of the weight of the tetramethylammonium hydroxide water solution. The result line width of the 0.7-micrometer mask pattern image in the same light exposure was measured using the electron microscope, and it asked for the magnitude of change of the result line width to thickness change of the photoresist film. A result is shown in a table -1.

[0045] The same with example of comparison 1Nafion (trademark) not being used, and also it being in an example 1, the surface acid-resisting spreading constituent (B) was prepared, and the shape of spreading membranous [of this] was observed, and the refractive index was measured. Moreover, dissolution detachability was observed like the example 1. A result is shown in a table -1.

[0046] The same with example of comparison 2Nafion (trademark) having been replaced with the polyvinyl pyrrolidone (ruby toast [; / by BASF A.G.] K-90), and also it being in an example 1, the surface acid-resisting spreading constituent (C) was prepared, and the shape of spreading membranous [of this] was observed, and the refractive index was measured. Moreover, like the example 1, dissolution detachability was observed and it asked for the magnitude of change of the result line width to change of photoresist thickness. A result is shown in a table -1.

[0047] The tetramethylammonium salt of an example of comparison 3 heptadeca fluoro octane sulfonic acid to the ammonium salt of a PENTA deca fluoro octanoic acid Nafion (trademark) to an alpha-perfluoro-NONENIRU-omega-methoxy polyoxyethylene (CH₃ : C₉F₁₇O-(CH₂CH₂O)₂₀-; made from NEOSU FUTAJIENTO -250) The same with it having replaced with, respectively and also being in an example 1, the surface acid-resisting spreading constituent (D) was prepared, and the shape of spreading membranous [of this] was observed, and the refractive index was measured. Moreover, the development omission pattern of dissolution detachability and 10-micrometer angle and the 1-micrometer line & tooth-space pattern were observed like the example 1. A result is shown in a table -1.

[0048] The surface acid-resisting spreading constituent (E) was prepared the same with having replaced

the tetramethylammonium salt of an example of comparison 4 heptadeca fluoro octane sulfonic acid with the ammonium salt of a PENTA deca fluoro octanoic acid, and Nafion (trademark) having been replaced with polyacrylic acid, respectively, and also it being in an example 1, and the shape of spreading membranous [of this] was observed, and the refractive index was measured. Moreover, the development omission pattern of dissolution detachability and 10-micrometer angle and the 1-micrometer line & tooth-space pattern were observed like the example 1. A result is shown in a table -1. [0049] the mixing ratio of the tetramethylammonium salt of an example of comparison 5 heptadeca fluoro octane sulfonic acid, and a polyvinyl pyrrolidone -- the same with the rate having been replaced with the weight ratios 7:3-8:2, and also it being in the example 2 of a comparison, the surface acid-resisting spreading constituent (F) was prepared, and the shape of spreading membranous [of this] was observed, and the refractive index was measured. Moreover, dissolution detachability as well as the example 2 of a comparison was observed. A result is shown in a table -1.

[0050]

[A table 1]

表 ー 1

	塗布膜性状	屈折率	溶解 剝離性	10μm角の 現像抜き パターン	1μmのライン & スペース	フォトレジスト膜厚 に対する仕上がり線 巾の変化
実施例 1	良 好	1.35	良 好	現像残りの パターンはな く、異常はな し	パターンの剥離が よく、現像残 りも少なく、解像 度も良好	小
比較例 1	袖子肌 のよ うな 荒れ に いた	測定不能	良 好	—	—	—
比較例 2	良 好	1.42	良 好	—	—	大
比較例 3	良 好	1.39	良 好	現像残りの パターンはな く、異常はな し	パターンの剥離が よく、ハネ がシリコ ンから剥離 し、多ク ハネが ハネ	—
比較例 4	良 好	1.42	良 好	現像残りの パターンはな く、異常はな し	現像残りの剥離が 多く、ハネが ハネ	—
比較例 5	塗布膜中に 微粒子が 散在した	1.40	良 好	—	—	—

* 1 : 相対評価。ただし、比較例 2 においても、表面反射防止塗布組成物を塗布しなかった場合に比べ、フォトリジスト膜厚の変化に対する仕上がり線巾の変化は小さかった。

[0051]
[Effect of the Invention] According to this invention, it has a low refractive index suitable as a surface antireflection film of a photoresist, and an aqueous medium can remove, a foreign matter is not generated in the spreading film, either, but the constituent for forming very few surface antireflection films of generating of the residue after development can be offered.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The typical sectional view showing the principle of relief of the film Uchida pile echo by the antireflection film.

[Description of Notations]

20 Exposure Light

21 Antireflection Film

22 Photoresist Film

23 Substrate

24 1st Reflected Light

25 Interface of Antireflection Film and Its Outside

26 Interface of Antireflection Film and Photoresist Film

27 2nd Reflected Light

28 3rd Reflected Light

[Translation done.]